

100 Years of Superconductivity

Part I

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Abstract

Superconductivity is a phenomenon of exactly zero electrical resistance occurring in certain materials below a characteristic temperature. It was discovered by Heike Kamerlingh Onnes in 1911 at Leiden in Netherlands. Like ferromagnetism and atomic spectral lines, superconductivity is a quantum mechanical phenomenon in macroscopic scale. It is characterized by a) Zero resistance b) Persistent Current c) Perfect diamagnetism d) Flux quantization and e) Energy gap. Several unsuccessful attempts were made since early 1930s to explain the phenomena even by physicists like Bohr, Heisenberg and Feynman, until the Theory of Superconductivity was cracked by Bardeen, Cooper and Schrieffer in 1957 in the USA. In the meantime, important contributions towards understanding the superconductivity was made by Meissner & Ochsenfeld, London & London, Fröhlich, Maxwell, Reynolds and a group of Soviet physicists including Landau, Ginzburg, Abrikosov, Gorkov, Bogolyubov and others. In 1960s, another milestone, the Josephson Tunneling, was reached. Until recently, because of the cryogenic requirements of very low-temperature, superconductivity was merely an interesting topic occasionally discussed in physics classes. With the discovery of high- T_c superconductors, which can operate at liquid nitrogen temperatures (77 K), superconductivity is now well within the scope for practical applications. Even, high school students can explore and experiment with this new and important technological field of physics. The Part I of this two part article traces the bumpy ride towards the understanding of the theory of superconductivity from 1911 to about 1957. The second part will discuss the aftermath of BCS theory, Type II superconductors, Josephson Effect, high T_c superconductivity, recent developments and some applications.

Discovery

The story of superconductivity can be traced back to the early 19th century with scientists being able to liquefy gases. In 1823, Faraday discovered that gaseous chlorine could be liquefied by generating it at high pressure at one end of a sealed glass tube and cooling it at the other end. With a good understanding of the science behind the liquefaction, Faraday set out to liquefy every known gas. His method and instruments were crude; nevertheless, he succeeded in liquefying every known gas, with three exceptions: oxygen, nitrogen, and hydrogen. In 1877, French



Fig 1. Heike Kamerlingh Onnes

physicist Louis P. Cailletet and Swiss scientist Raoul P. Pictet independently succeeded in liquefying both oxygen and nitrogen. But their yield was very small. Before that achievement, many in the scientific community assumed that those gases, along with hydrogen, were perhaps beyond

liquefaction. By 1883, Karol Olszewski and Zygmunt von Wroblewski in Cracow had succeeded in collecting cubic centimeters of liquid oxygen, and nitrogen. In 1892, Heike Kamerlingh Onnes, a young professor of Leiden University, succeeded in developing an apparatus for producing those in large quantities. The system took advantage of what became known as the cascade process. The only gas remaining to be conquered was hydrogen, as helium was unknown, although its existence in the Sun was known. The liquefaction of hydrogen developed into a bone of contention between Heike Kamerlingh Onnes and Sir James Dewar, the Scottish low-temperature physicist. In 1898, Dewar, succeeded to liquefy hydrogen by taking advantage of a thermodynamic effect known as Joule-Thomson expansion.

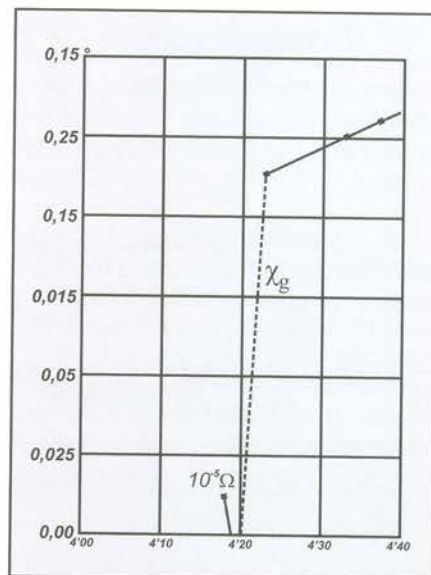


Fig 2. Kammerling Onnes' original plot of superconducting transition of Mercury.

Losing the race for liquefying hydrogen to Dewar, Onnes developed the first helium liquefier in 1908. (Interestingly, Helium on the Earth was discovered only in 1895 by the English chemist William Ramsay). On July 10, 1908, he successfully liquefied helium by cooling it to 269 degrees below zero degrees Celsius (4 Kelvin or 4 K). The discovery opened the door to an entire realm of possibility involving low temperature experiments. This was the first successful attempt at liquefying helium which provided a new temperature range approaching absolute zero. Kamerlingh-Onnes pioneered work at very low temperatures just a few degrees above the absolute zero of temperature. He succeeded in reaching temperatures much colder than anyone before him and thus opened a new frontier for science, the field of low temperature physics. He and co-researchers Gilles Holst, a student entrusted by Onnes with precise resistance measurements, and G. J. Flim, the technician responsible for the helium liquefier itself, performed the experiments to study what happened to various properties of materials when they were extremely cold. Holst was studying the electrical resistance of wires. He found that as he cooled mercury wire, the electrical resistance of the wire took an abrupt drop when he got to about 3.6 degrees above absolute zero. The drop was enormous - the resistance became at least twenty thousand times smaller. The drop took place over a temperature interval too small for them to measure. As far as they could tell, the electrical resistance completely vanished.

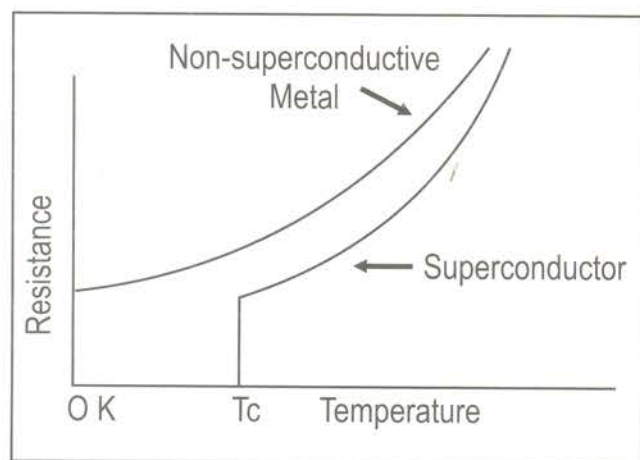


Fig 3. Low temperature plot of resistance versus temperature in Normal and Superconducting materials

Previous tests had found that the resistances fell exponentially as the temperature approached zero. It had been known for many years that the resistance of metals fell when cooled below room temperature, but

it was not known what limiting value the resistance would approach, if the temperature were reduced to very close to 0 K. Some scientists, such as William Kelvin, believed that electrons flowing through a conductor would come to a complete halt as the temperature approached absolute zero. Other scientists, including Kamerlingh-Onnes, felt that a cold wire's resistance would dissipate. This suggested that there would be a steady decrease in electrical resistance, allowing for better conduction of electricity. At some very low temperature point, scientists felt that there would be a leveling off as the resistance reached some ill-defined minimum value allowing the current to flow with little or no resistance. However, the testing of mercury broke the notion. Onnes found that at 4.2 degrees Kelvin, the resistance of mercury fell sharply. Later Kamerlingh-Onnes described the phenomenon as:

"At this point (somewhat below 4.2 K) within some hundredths of a degree came a sudden fall not foreseen by the vibrator theory of resistance, that had been framed, bringing the resistance at once less than a millionth of its original value at the melting point... Mercury had passed into a new state, which on account of its extraordinary electrical properties may be called the superconductive state."

Fig (1) shows Onnes' original graph presented during his Nobel Lecture. To explain why resistivity depended on temperature at all, Onnes embraced Albert Einstein's recent theory of quantum oscillators, devised in 1906 to explain the observed specific heats of solids. If the thermal oscillations of atoms were what impeded the flow of current, and these oscillations became smaller at low temperature as Einstein would predict, then Einstein's oscillators might explain the way resistance diminished in metals at low temperature. This picture predicted that, rather than increase to infinity as the temperature approached 0K, the resistivity of a pure metal would fall toward zero. To test his idea, Onnes chose mercury, which could be purified by distillation, and which was expected to have a high enough resistance to measure at 4 K.

Repeated trials convinced Onnes that the sudden loss of mercury's resistance at about 4.2 K was real. The result was first presented by Onnes at the first Solvay Conference, held in Brussels from October 30th to November 3rd, 1911 under the title *"On the Sudden Change in the Rate at Which the Resistance of Mercury Disappears"*. He reported the work of his laboratory under his own name alone, without co-authors. Holst never got credit for discovering superconductivity.

Subsequent tests of tin and lead showed that superconductivity was a property of numerous metals if they were cooled sufficiently. Figure (2) is a graph of resistance versus temperature in normal as well as Superconducting materials.

By 1914 Onnes established a permanent current, or what he called a "persistent super current," in a superconducting coil of lead. The coil was placed in a cryostat at low temperature, with the current being induced by an external magnetic field. With no resistance, the electrons in the coil were free to continue to flow indefinitely. In one of Kamerlingh-Onnes experiments, he started a current flowing through a loop of lead wire cooled to 4 K. A year later the current was still flowing without significant current loss. Onnes noted that the state could be destroyed by applying a sufficiently large magnetic field while a current induced in a closed loop of superconducting wire persisted for an extraordinarily long time. He demonstrated the latter phenomenon by starting superconducting current in a coil in his Leiden laboratory and then transporting the coil plus the refrigerator, which kept it cold, to Cambridge University for a lecture demonstration on superconductivity. Physicists were making pilgrimages to Leiden to observe the inconceivable: a persistent current in a loop of superconducting wire, interacting with a common magnet needle.

Onnes's report did not cause much stir at that time, but Onnes recognized the importance of his discovery to the scientific community as well as its commercial potential. An electrical conductor with no resistance could carry current to any distance with no losses. In his Nobel Prize speech in 1913 (the prize was awarded

for his researches on helium), Onnes underlined the unexpected, abrupt nature of the decrease in resistance. By 1913, it was established that the same phenomenon, now called "the super-conducting state," occurred in lead and tin, but not gold and platinum. In subsequent decades other superconducting metals, alloys and compounds were discovered. In 1941 niobium-nitride was found to super conduct at 16 K. In 1953 vanadium-silicon displayed superconductive properties at 17.5 K. And, in 1962 scientists at Westinghouse developed the first commercial superconducting wire, an alloy of niobium and titanium (NbTi). [Table 1 shows Superconducting Transition Temperature for some metals].

Meissner Effect: The Next Revolution



Fig 4. Walther Meissner

The First World War brought a temporary break in low temperature research. Helium became unavailable in Europe. It restarted in 1919 with a gift of 30 cubic meter Helium coming from the USA. Helium was abundant in the United States. The Leiden group resumed work on superconductivity, discovering a number of new superconducting elements (thallium, indium, etc.), and also studying the magnetic properties of superconductors. In 1923 helium was liquefied in Toronto under J. C. McLennan. Two years later, in 1925, Walther Meissner in Berlin started liquid-helium research. He was eager to join Onnes' group in Leiden, but finally formed his own group. The research at Berlin was remarkable discovering whole new classes of superconducting elements, alloys and chemical compounds.

In 1933, Max von Laue, the German Nobel Laureate, suggested to Meissner an experiment designed to determine whether the current in a superconductor flows on its surface or in its bulk. Meissner chose Robert Ochsenfeld to carry out the experiment. To their surprise they found that a superconducting material repels a magnetic field and excludes it completely from its bulk. This means that if you bring a small bar magnet up to a superconductor, the superconductor bends the lines of force away from it and doesn't allow them to penetrate. This phenomenon is known as perfect diamagnetism and is today often referred to as the "Meissner effect" and is a very popular demonstration of superconductivity. The Meissner Effect is so strong that a magnet can actually be levitated.

Metals	Transition temperature
Lead (Pb)	7.196 K
Lanthanum (La)	4.88 K
Tantalum (Ta)	4.47 K
Mercury (Hg)	4.15 K
Tin (Sn)	3.72 K
Indium (In)	3.41 K

Table 1: Superconducting Transition Temperature for some metals

over a superconductive material. The Meissner Effect will occur only if the magnetic field is relatively small. If the magnetic field becomes too great, it penetrates the interior of the metal and the metal loses its superconductivity. The magnetic field vanishes in the interior of a bulk specimen, even when cooled down below the transition temperature in the presence of a magnetic field. The diamagnetic currents which flow in a thin penetration layer near the surface of a simply connected body to shield the interior from an externally applied field are stable rather than metastable. On the other hand, persistent currents flowing in a multiply connected body, e.g., a loop, are metastable.

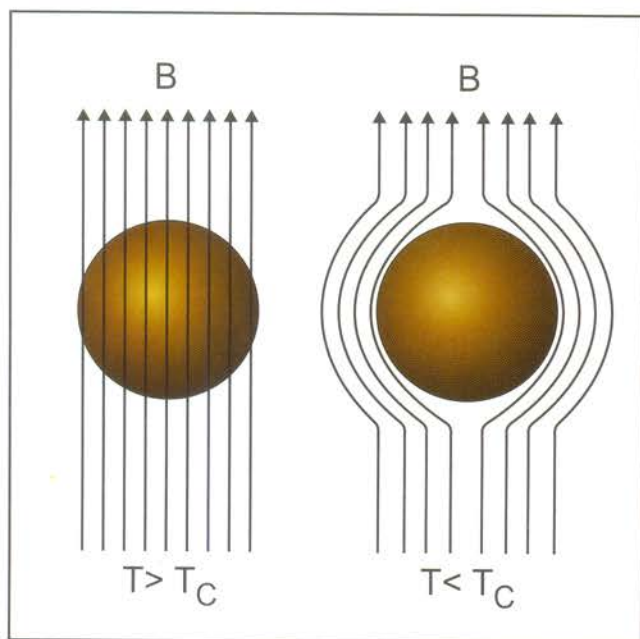


Fig 5: Diamagnetic property of a superconductor

An American, F. B. Silsbee, had suggested (using Leiden data), that the observed breakdown of superconductivity in a magnetic field was sufficient to explain why superconductivity was also destroyed when the sample carried a very large electric current: the current simply created the necessary magnetic field. The Leiden group verified Silsbee's hypothesis. They also developed the strong conviction that, when a sample became superconducting, whatever magnetic flux was already around became frozen in, and all other changes in flux through the sample would be excluded by the perfect conductivity. Thus the magnetic state of the sample was not reversible, so that no thermodynamic analysis could be applied. The result was dramatic and unexpected: even when the tin cylinders were not carrying any current, the magnetic field between them increased when they were cooled

into their superconducting state. The frozen-in flux idea was not correct, and the exclusion of applied flux was not merely a dynamical effect of perfect conductivity. Superconductors were not only perfect conductors, they were also perfect diamagnets. Mathematically, we obtain a particularly useful form of this result if we limit ourselves to long thin specimens with long axis parallel to B_a ; now the demagnetizing field contribution to B will be negligible, whence:

$$B = B_a + 4\pi M = 0 \quad \text{or} \quad \frac{M}{B_a} = -\frac{1}{4\pi}$$

The result $B=0$ cannot be derived from the characterization of a superconductor as a medium of zero resistivity. From Ohm's law, $E = \rho j$, it can be easily shown that if the resistivity ρ goes zero while j finite, then E must be zero. By Maxwell's eqn. dB/dt is proportional to $\text{curl } E$, so that zero resistivity implies $dB/dt = 0$. This predicts that the flux through the metal cannot change on cooling through the transition. The Meissner effect contradicts this result and suggests that perfect diamagnetism is an essential property of the superconducting state.

Electrical & Magnetic Properties of Superconductors

Since there is no loss in electrical energy when superconductors carry electrical current, relatively narrow wires made of superconducting materials can be used to carry huge currents. However, there is a certain maximum current that these materials can be made to carry, above which they stop being superconductors. If too much current is pushed through a superconductor, it will revert to the normal state even though it may be below its transition temperature. The value of **Critical Current Density** (J_c) is a function of temperature; i.e., the colder you keep the superconductor the more current it can carry. For practical applications, J_c values in excess of 1000 amperes per square millimeter (A/mm) are preferred.

An electrical current in a wire creates a magnetic field around a wire. The strength of the magnetic field increases as the current in the wire increases. Because superconductors are able to carry large currents without loss of energy, they are well suited for making strong electromagnets. When a superconductor is cooled below its **transition temperature** (T_c) and a magnetic field is increased around it, the magnetic field remains around the superconductor. Physicists use the capital letter H as the symbol for **Magnetic Field**. If the magnetic field is increased to a given point the superconductor will go to the normal resistive state.

The maximum value for the magnetic field at a given temperature is known as the **Critical magnetic field** and is given the symbol H_c . For all superconductors there exists a region of temperatures and magnetic fields within which the material is superconducting. Outside this region the material is normal.

When the temperature is lowered to below the critical temperature, (T_c), the superconductor will "push" the field out of itself. It does this by creating surface currents in itself which produces a magnetic field exactly countering the external field, producing a "magnetic mirror". The superconductor becomes perfectly diamagnetic, canceling all magnetic flux in its interior. This perfect diamagnetic property of superconductors is perhaps the most fundamental macroscopic property of a superconductor. Flux exclusion due to what is referred to as the Meissner Effect, can be easily demonstrated in the classroom by lowering the temperature of the superconductor to below its T_c and placing a small magnet over it. The magnet will begin to float above the superconductor. In most cases the initial magnetic field from the magnet resting on the superconductor will be strong enough that some of the field will penetrate the material, resulting in a non-superconducting region. The magnet, therefore, will not levitate as high as one introduced after the superconductive state has been obtained.

Early Attempts Towards an Explanation

Before the discovery of the Meissner effect, attempts to make theoretical progress in explaining superconductivity, particularly by applying the newly created quantum theory, made little progress. In reality, there was no chance for anyone to solve this problem at the time of discovery because before one could explain it, one had to have the quantum theory in the form that Schrödinger and Heisenberg developed, which did not take place until the 1920's. For a long time the

phenomenon of superconductivity was characterized by the statement that the electrical resistance vanished completely. Albert Einstein in 1922 concluded that quantum theory was not yet up to the task.

Between 1929 and 1933 Felix Bloch, whose doctoral thesis in 1928 gave the basic theory of conductivity in metals, worked on the problem together with Wolfgang Pauli and Lev Landau. Niels Bohr, Werner Heisenberg and Léon Brillouin also joined the efforts, but without any success.

The discovery of the Meissner Effect was a crucial turning point. Superconductivity still could not be explained in terms of quantum mechanics, but the thermodynamics of the phenomenon was understandable. Paul Ehrenfest, who believed that superconductivity could be treated as a thermodynamic phase transition, sent his former student Hendrik Casimir to Leiden, where in 1934 he joined Cornelius Gorter, a student of W. J. de Haas. The two of them succeeded in proving Ehrenfest correct, producing the results that are found today in every textbook. Casimir and Gorter advanced a two fluid model to account for the observed second order phase transition at T_c and other thermodynamic properties. They proposed that the total density of electrons ρ could be divided into two components $\rho = \rho_s + \rho_n$ where a fraction ρ_s/ρ_n of the electrons can be viewed as being condensed into a "superfluid," which is primarily responsible for the remarkable properties of superconductors, while the remaining electrons form an interpenetrating fluid of "normal" electrons. The fraction ρ_s/ρ_n grows steadily from zero at T_c to unity at $T = 0$, where "all of the electrons" are in the superfluid condensate.

A second important theoretical advance came in the following year, when brothers Fritz and Hans London, two refugees from Nazi Germany, at the Clarendon Laboratory at Oxford, proposed their phenomenological theory of the electromagnetic properties of superconductors, in which the diamagnetic rather than electric aspects were assumed to be more fundamental. In an ordinary metal we describe the phenomenon of electrical resistance by the famous Ohm's law. What the London brothers did was to show that there was another mathematical relationship which should be used in place of Ohm's law to describe superconductors. From this other relationship which they developed, they were able to explain both the Meissner-Ochsenfeld experiment as well as the persistent current of Kamerlingh-Onnes as two manifestations of the same thing.

They suggested that the electrical current density $\mathbf{j}$, carried by the superfluid is related to the electric field $\mathbf{E}$



Fig 6. Fritz and Hans London

and magnetic field $\mathbf{B}$ at each point in space by two London equations expressed in terms of measurable fields:

$$\frac{\partial \mathbf{j}_s}{\partial t} = \frac{n_s e^2}{m} \mathbf{E}, \quad \nabla \times \mathbf{j}_s = -\frac{n_s e^2}{mc} \mathbf{B}.$$

Here $\mathbf{j}_s$ is the superconducting current, $\mathbf{E}$ and $\mathbf{B}$ are respectively the electric and magnetic fields within the superconductor, e is the charge of an electron & proton, m is electron mass, and N_s is a phenomenological constant loosely associated with a number density of superconducting carriers.

The two equations can be combined to form a single "London Equation" in terms of the magnetic vector potential $\mathbf{A}$:

$$\mathbf{j}_s = -\frac{n_s e^2}{mc} \mathbf{A}.$$

$\mathbf{A}$ is to be chosen such that $\nabla \cdot \mathbf{A} = 0$ to ensure current conservation. If the second of London's equations is manipulated by applying Ampere's law

$$\nabla \times \mathbf{B} = \frac{4\pi \mathbf{j}}{c}$$

then the result is the differential equation

$$\nabla^2 \mathbf{B} = \frac{1}{\lambda^2} \mathbf{B}, \quad \lambda = \sqrt{\frac{mc^2}{4\pi n_s e^2}}$$

Therefore, $\mathbf{B}(x) = \mathbf{B}_0 e^{-x/\lambda}$.

Thus, the London equations imply a characteristic length scale, λ , over which external magnetic fields are exponentially suppressed. This value is the London penetration depth. It follows that a magnetic field is excluded from a superconductor except within a distance which is of order of 10^{-6} cm in typical superconductors for T well below T_c . Observed values of λ are however several times the London value.

From London theory, the important phenomena of flux quantization can be easily understood. We consider here a superconducting ring. Deep in the interior of the superconductor, the magnetic field is completely screened out, and therefore, super currents should be absent there i.e.,

$$\oint \mathbf{j}_s \cdot d\mathbf{l} = 0$$

Introducing super current density and rearranging we get

$$\oint \mathbf{A} \cdot d\mathbf{l} = \iint \mathbf{B} \cdot d\mathbf{S} = \phi_s$$

is the magnetic flux through the ring. We see then, that the magnetic flux is quantized

$$\phi_s = n \frac{2\pi\hbar c}{e^*} n \phi_0$$

in units of the flux quantum $\phi_0 = \frac{\hbar c}{e^*}$

In the same year (1935) Fritz London suggested how the diamagnetic property might follow from quantum mechanics, if the wavefunction ψ of the superconducting state essentially remains unchanged by the presence of an externally applied magnetic field. This concept is basic to the theoretical development since that time, in that it sets the stage for the gap in the excitation spectrum of a superconductor which separates the energy of superfluid electrons from the energy of electrons in the normal fluid. Fritz London moved to USA in 1939 and in his book published in 1950, he extended his theoretical conjectures by suggesting that a superconductor is a "quantum structure on a macroscopic scale [which is a] kind of solidification or condensation of the average momentum distribution" of the electrons. This momentum space condensation locks the average momentum of each electron to a common value which extends over appreciable distance in space. London's book included very perceptive comments about the nature of the microscopic theory that have turned out to be remarkably accurate. He suggested that superconductivity requires "a kind of solidification or condensation of the average momentum distribution." He also predicted the phenomenon of flux quantization, which was not observed till 1960s or so. In 1940s David Schoenberg (the Russian-English Physicist at Cambridge) and John Bardeen in the USA also floated theories for explaining superconductivity but without any success.

Development Between 1950-57

The Second World War interrupted research in superconductivity just as the First World War had done. It was not until about 1950 that real progress began once again to be made. The phenomenon still resisted any true microscopic understanding, but some pieces of the puzzle did begin to come together, particularly in the phenomenological model of Vitaly Ginzburg and Lev Landau. Ginzburg and Landau (1950) extended the London phenomenology in a brilliant stroke based on Landau's theory of second-

order phase transitions. It does not purport to explain the microscopic mechanisms giving rise to superconductivity. Instead, it examines the macroscopic properties of a superconductor with the aid of general thermodynamic arguments. This theory is sometimes called phenomenological as it describes some of the phenomena of superconductivity without explaining the underlying microscopic mechanism. Based on Landau's previously-established theory of second-order phase transitions, Landau and Ginzburg argued that the free energy F of a superconductor near the superconducting transition can be expressed in terms of a complex order parameter ψ , which describes how deep into the superconducting phase the system is. The free energy has the form where F_n is the free

$$F = F_n + \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2m} |(-i\hbar\nabla - 2e\mathbf{A})\psi|^2 + \frac{|\mathbf{B}|^2}{2\mu_0}$$

energy in the normal phase, α and β are phenomenological parameters, m is an effective mass, e is the charge of an electron, $\mathbf{A}$ is the magnetic vector potential, and $\mathbf{B} = \text{curl}(\mathbf{A})$ is the magnetic field. By minimizing the free energy with respect to fluctuations in the order parameter and the vector potential, one arrives at the **Ginzburg-Landau equations**

$$\alpha\psi + \beta|\psi|^2\psi + \frac{1}{2m}(-i\hbar\nabla - 2e\mathbf{A})^2\psi = 0$$

$$\mathbf{j} = \frac{2e}{m} \text{Re} \{ \psi^* (-i\hbar\nabla - 2e\mathbf{A})\psi \}$$

where $\mathbf{j}$ denotes the electrical current density and Re the real part. The first equation, which bears interesting similarities to the time-independent Schrödinger equation, determines the order parameter ψ based on the applied magnetic field. The second equation then provides the superconducting current. This theory was later shown by Gor'kov (1959) to be a limiting case of the BCS theory and remains today as the standard initial approach to problems with a spatially varying superconducting state. The real significance of the wave function-like order parameter would not be explained until the microscopic BCS theory came along towards the end of the decade. However, even after the BCS theory provided a microscopic understanding of superconductivity, the much simpler and easier-to-use Ginzburg-Landau model remained (and remains) the every-day working theory used by theorists and experimentalists alike to analyze all manner of complex phenomena in superconductivity.



Fig 7. Vitaly Ginzburg (left) and Lev Landau

An important concept was introduced by A. B. Pippard in 1953. Aided by wartime development in high-frequency technology, Pippard was able to make very precise measurements of λ_L to compare with London Equation, using parameters determined from similar measurements of the skin depth in the normal state of metals. He found that, even at $T \sim 0$, the fitted value of n_s was less than the density of conduction electrons in the normal state, by a ratio that was larger for low- T_c materials like Al ($T_c \approx 1$ K) than for metals like Pb ($T_c \approx 7$ K). He concluded that a "coherence length" ξ_0 is associated with the superconducting state such that a perturbation of the superconductor at a point necessarily influences the superfluid within a distance ξ_0 of that point. For pure metals, $\xi_0 \sim 10^{-4}$ cm. for $T < T_c$. He generalized the London equation to a non-local form and accounted for the fact that the experimental value of the penetration depth is several times larger than the London value. Subsequently, Bardeen showed that Pippard's non-local relation would likely follow from an energy gap model.

Perhaps the single most important experiment which directly played a guiding role to an explanation of superconductivity was the experiment on the "isotope effect." This occurred in the spring of 1950. Papers from two laboratories simultaneously revealed the same results. One paper was by Reynolds, Serin, Wright and Nesbitt at Rutgers University. The other was by E. Maxwell at the U. S. National Bureau of Standards. Both groups measured the transition temperatures of separated mercury isotopes and found that in mercury T_c varies from 4.185K to 4.146K as the average atomic mass M varies from 199.5 to 203.4 a.m.u. The transition temperature changes smoothly as different isotopes of a same element mixed. This result behaves to the relation- **$M^{-1}T_c = \text{Constant}$** .

Substance	α
Cd	0.32±0.07
Hg	0.50±0.03
Pb	0.49±0.02
Zn	0.45±0.05
Zr	0.00±0.05

Table 2. Observed values of α for isotope effect in superconductors

From the above relation and data between T_c and isotopic mass, we can understand that lattice vibration and electron-lattice interactions are closely related to superconductivity. So what the isotopic experiments we've just talked about showed was that although the electrical conductivity was known to arise because of the motion of the electrons, there's some role of these lattice vibrations. They enable the electrons suddenly to move through the lattice, evidently without hindrance, when the sample is cooled to the critical superconducting temperature.

It was the elementary discovery that transition temperature depends on number of nucleons. If the mass of the ions is important, their motion and thus the lattice vibrations must be involved. Independently, British physicist Herbert Fröhlich, who was then spending the spring term at Purdue University, attempted to develop a theory of superconductivity based on the self-energy of the electrons in the field of phonons. He heard about the isotope effect in mid-May, shortly before he submitted his paper for publication and was delighted to find very strong experimental confirmation of his ideas. He used a Hamiltonian, now called the Fröhlich Hamiltonian, in which interactions between electrons and phonons are included but Coulomb interactions are omitted except as they can be included in the energies of the individual electrons and phonons. Fröhlich used a perturbation theory approach and found instability of the Fermi surface if the electron-phonon interaction were sufficiently strong. Herbert Fröhlich realized that the observation that good conductors (copper, gold) tend not to become superconductors might mean that superconductivity is produced by a relatively strong interaction between the conduction electrons and the lattice vibrations, or phonons, in those metals that were not good normal conductors.

The next big experimental discovery was done by two groups: Goodman, who was making thermal conductivity experiments, and Brown, Zemansky and Boorse, who were making specific heat measurements. They discovered what is called the energy gap.

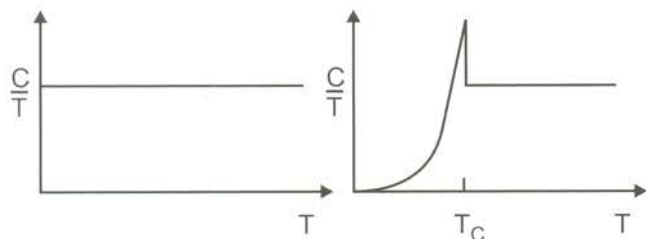


Fig 8. Temperature variation of electronic specific heat of normal metal (left) and superconductor

The specific heat of a solid C_v can be expressed as $C_v = \gamma T + \alpha T^3$, where the first term is the electronic contribution (predominant for good metals at very low temperature) and the second term is the lattice contribution. The graph above left shows the behavior of normal metal while that in the right shows the behavior in the superconducting state. The surprising feature of the curve is that below T_c the C_v falls as $e^{-\Delta/kT}$ indicating a clear gap in the electronic energy spectrum. The possible energy levels for electrons free to move about a volume V are found from the Schrödinger equation. The energy levels are quantized, and each level (ϵ) can be occupied by two fermions, one with spin up and one with spin down. At $T=0$, the energy levels will be completely filled up to a certain energy, which is called the Fermi energy, ϵ_F . At $T=0$, there will be no occupied states with $\epsilon > \epsilon_F$. In metals in normal state, electrons move above the Fermi Energy at $T > 0$ K. But in superconducting state this is not easy; you need to impart sufficiently more energy to overcome an energy gap above the Fermi Energy. It was a vital clue towards cracking the theory of superconductivity.

Thus by 1955-56, two indications were clear: the electron phonon interaction and energy gap. But a comprehensive theory was still eluding scientists. Meanwhile, Schafroth showed that starting with the Fröhlich Hamiltonian, one cannot derive the Meissner effect in any order of perturbation theory. Russian physicist Migdal's theory, supposedly correct to terms of order $(m/M)^{1/2}$, gave no gap or instability at the Fermi surface and no indication of superconductivity.

Bob Schrieffer summarized the situation as "This was the state of our understanding of the electrodynamics of classic superconductors in the mid-1950s—a very satisfactory phenomenology, but no "explanation" in microscopic terms. What was the nature of the superconducting state that made it have these remarkable properties? This question was answered in one stroke by the classic paper of Bardeen, Cooper, and Schrieffer (1957) ..."

Events Leading to the BCS Theory

The man who led the path breaking research leading to a satisfactory explanation to the phenomenon of superconductivity was John Bardeen. Bardeen recalls that "My first introduction to superconductivity came in the 1930's and I greatly profited from reading David Shoenberg's little book on superconductivity, which gave an excellent summary of the experimental findings and of the phenomenological theories that had been developed". Bardeen's first abortive attempt to

construct a theory, in 1940, was strongly influenced by London's ideas and the key idea was small energy gaps at the Fermi surface arising from small lattice displacements. However, this work was interrupted by several years of wartime research, and then after the war Bardeen joined the group at the Bell Telephone Laboratories where his work turned to semiconductors. Bardeen came to University of Illinois at Urbana in the early 1950's as jointly a professor of physics and a professor of electrical engineering at the former Bell Laboratories where he, Walter Brattain, and William Shockley invented the transistor. It was not until then, as a result of the discovery of the isotope effect that Bardeen again began to become interested in Superconductivity. Bardeen heard about the isotope effect in early May, 1950 in a telephone call from Serin, and realized that the isotope effect identified the interaction between electrons and phonons that must be responsible for the phenomenon. The basic idea would be a Fermi-degenerate gas of nearly free electrons, with a weakly attractive interaction by way of the lattice phonons. He attempted to revive his earlier theory of energy gaps at the Fermi surface, with the gaps now arising from dynamic interactions with the phonons rather than from small static lattice displacements. Bardeen used a variational method rather than a perturbation approach but the theory was also based on the electron self-energy in the field of phonons. At the same time, Bardeen and Fröhlich independently put forward theories of superconductivity which later on turned out to be incorrect. It became evident that nearly all of the self-energy is included in the normal state and is little changed in the transition. A theory involving a true many-body interaction between the electrons seemed to be required to account for superconductivity. However, both of them said they thought an essential portion of the problem had to do with what happened to the electrons whose energy was equal to the Fermi energy. The interaction studied by Fröhlich is at first sight quite appealing, being both novel and potentially involving the right dependence on the isotopic mass. There was however a major problem in understanding how it could play a role, since the basic Coulomb interaction between electrons is both repulsive and very much stronger. As Landau put it "you can't repeal Coulomb's law."

In 1955, stimulated by writing a review article on the status of the theory of superconductivity, John Bardeen decided to renew the attack on the problem. Solving that problem proved to be a difficult task. There was also the threat of powerful competition. Richard Feynman, one of the masters of quantum electrodynamics, and renowned Soviet Physicists like Landau and Bogolyubov were close to the solution. In quantum electrodynamics, electrons in vacuum interact with one

another via photons, or quantized light waves. In the model Bardeen was trying to solve, electrons in metals interact with one another via phonons, or quantized lattice vibrations. This was the problem which John Bardeen and David Pines, his post-doc fellow at the University of Illinois during the period 1952-55, attacked. What they found by extending an approach which David Bohm and David Pines had earlier developed for understanding the consequences of electron-electron interactions in metals, was that the medium is the message. When they took into account the influence of electronic screening processes on both electron-electron and electron-ion interactions, they found that the presence of a second component, the ions, makes possible a net attractive interaction between a pair of electrons whose energy difference is less than a characteristic phonon energy.



Fig 9. Bardeen (left), Cooper (center) and Schrieffer

In 1955, when Pines left University of Illinois, Bardeen decided that reinforcements were needed. He called up C. N. Yang at the Institute for Advanced Study at Princeton, to ask for a postdoc versed in the field theory. Yang recommended Leon Cooper since Cooper's background was in particle physics. Cooper had recently completed his PhD in particle physics and in the process he had learned a set of mathematical techniques called quantum field theory. He was viewed as one of the best young men in the subject. Bardeen felt it might be important to know these techniques in order to tackle the problem of superconductivity. So he

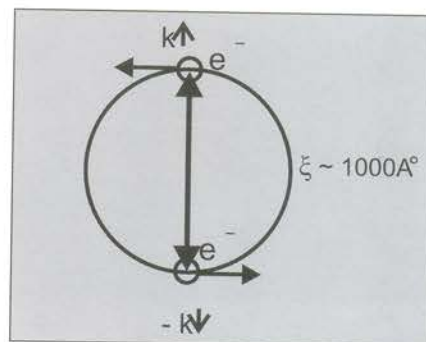


Fig. 10. Schematic representation of a Cooper Pair.

invited Cooper to come to Urbana. Because of his mastery in quantum mechanics he was jokingly called by others in the department as "*Bardeen's quantum mechanic*". Meanwhile, Bob Schrieffer was at the University of Illinois as a graduate student. He had completed his undergraduate studies at MIT, working in a group of solid state physicists. When he reached graduation time, he decided to work with Bardeen. Initially, Bardeen suggested some work on semiconductors. When it came time for a thesis, Schrieffer chose to work on superconductivity. The team was assembled at the University of Illinois physics department, Bardeen and Cooper had to share an office. In the meantime, Schrieffer worked in a room full of other graduate students. The situation was not conducive, but spirit of the trio was on high.

It soon became clear that since the existing field-theoretic methods were based on perturbation theory, another scheme would have to be devised. Bardeen stressed the importance of an energy gap in the excitation spectrum and that superconductivity is due to a condensation in momentum space of a coherent superposition of normal-state configurations. But it was difficult to explain quantitatively. Fortunately, Landau's theory of a Fermi liquid provided the necessary basis for treating the normal-state excitations in one-to-one correspondence with the free-electron gas so that the small condensation energy between the super and normal phases could be isolated.

The first major breakthrough this trio made in superconductivity came from Leon Cooper. Cooper was making an effort to find out why there was an

energy gap. Cooper studied the general theories of quantum mechanics and considered a simplified model of the interactions of two electrons. At very low temperature, all states up to Fermi level are filled and hence not available to these electrons. He then examined what considered : the first was that the Coulomb repulsion of electrons, because they are of the same charge. The second was that the electrons interact via lattice vibrations; one electron displaces a nucleus as it passes by the nucleus which in turn attracts another electron forming a pair of moving electrons. The interaction was energetically favorable - there was a net attraction.

Cooper concluded that superconductivity arose when the attractive interaction of one electron for the other, through the lattice, was larger than the direct repulsion. This then became a criterion for superconductivity. Cooper published a paper in 1956 and it is one of the famous papers in the history of superconductivity. The interacting pairs of electrons have since been known as "Cooper pairs" after their discoverer. It is interesting to note that in his 1956 paper, Cooper referred to Ginzburg and Scafrorth as saying that two electrons or even more, if grouped together and have zero or integral spin, would behave like Bosons.

At this point Bardeen, Cooper and Schrieffer decided to try to generalize Cooper's results to many electron systems. The trouble was that a Cooper Pair appeared to interact with a third or fourth electron unfavorably. They understood that a single Cooper pair was unstable. The break came when Bob Schrieffer succeeded in guessing the nature of the solution at absolute zero. They then attempted to generalize the solution to the higher temperatures, and to show that in fact they could account for all of the facts of superconductivity. The first joint paper of the group was published in February, 1957. This was the prelude to the final theory.

The trio then felt they were close to the success. But they still had lots to do. Bardeen went to Stockholm to collect his 1956 Nobel Prize while Cooper and Schrieffer engrossed into deep thinking and calculation. But within a few months they were successful. It became clear that the key to superconductivity is the condensation of all electron pairs into momentum space, that is, they will have same momentum (though they may be physically far apart) and can be described by a single wave function. It is easy to understand that such a situation may arise as the Cooper Pairs are Bosons and are not restricted by Pauli Exclusion Principle to occupy same energy states.

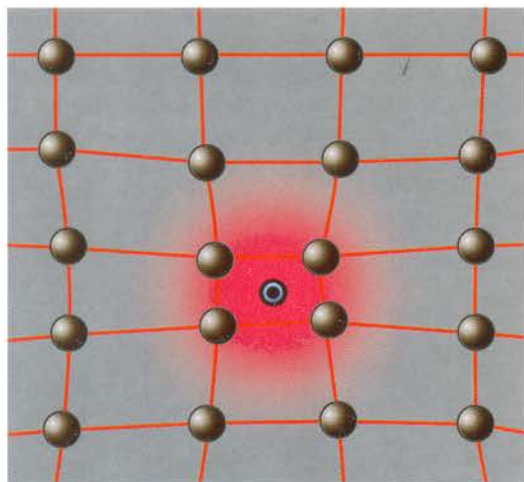


Fig 11. Electron Lattice interaction.

Their December 1957 paper (See Annexure I) successfully explained all aspects of Superconductivity. In 1972 John Bardeen, Leon Cooper and Bob Schrieffer were awarded the Nobel Prize in physics for their theory of superconductivity.

Salient Features of BCS Theory

- ♣ The electrons are bound into Cooper pairs, and these pairs form a Boson like condensate. In order to break a pair, one has to change energies of all other pairs. This means there is an "energy gap" for "single-particle excitation", unlike in the normal metal. This energy gap is highest at low temperatures but vanishes at the transition temperature when superconductivity ceases to exist.

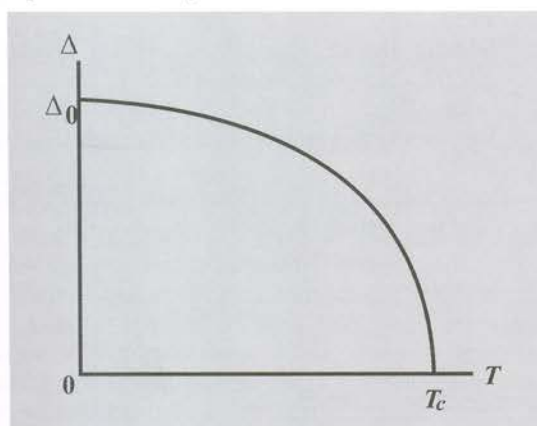


Fig 12. Variation of band gap with temperature.

- ♣ BCS theory predicts the dependence of the value of the energy gap, Δ at temperature T on the critical temperature T_c . The ratio between the value of the energy gap at zero temperature and the value of the superconducting transition temperature takes the universal value of 3.5, independent of material. Near the critical temperature the relation asymptotes to

$$E = 3.52 k_B T_c \sqrt{1 - (T/T_c)}$$

- ♣ Due to the energy gap, the specific heat of the superconductor is suppressed strongly at low temperatures, there being no thermal excitations left. However, before reaching the transition temperature, the specific heat of the superconductor becomes even higher than that of the normal conductor and the ratio of these two values is found to be universally given by 2.5.

$$C \sim \frac{\Delta^2}{T^2} \exp(-\beta/2\Delta)$$

- ♣ BCS theory correctly predicts the Meissner effect. It also describes the variation of the critical magnetic field with temperature. In its simplest form, BCS gives the superconducting transition temperature in terms of the electron-phonon coupling potential and the Debye cutoff energy:

$$k_B T_c = \beta_c^{-1} \approx 1.13 \hbar \omega_D \exp(-1/N(0) \lambda)$$

Here $N(0)$ is the electronic density of states at the Fermi energy. This shows that $T_c \sim \omega_D \sim M^{-1/2}$ explaining the isotopic effect.

[It being very complicated and not suitable for this paper, the author decides to avoid discussing the detail mathematics of BCS Theory. However, it must be kept in mind that important mathematical tools had been developed by several physicists who made the BCS calculation possible. One can find Bardeen's acknowledgement from his 1972 Nobel Lecture: "In 1950, diagrammatic methods were just being introduced into quantum field theory to account for the interaction of electrons with the field of photons. It was several years before they were developed with full power for application to the quantum statistical mechanics of many interacting particles. Following Matsubara, those prominent in the development of the theoretical methods include Kubo, Martin and Schwinger, and particularly the Soviet physicists, Migdal, Galitski, Abrikosov, Dzyaloshinski, and Gorkov. The methods were first introduced to superconductivity theory by Gorkov and a little later in a somewhat different form by Kadanoff and Martin. Problems of superconductivity have provided many applications for the powerful Green's function methods of many-body theory and these applications have helped to further develop the theory. Diagrammatic methods were first applied to discuss electron-phonon interactions in normal metals by Migdal and his method was extended to superconductors by Eliashberg. A similar approach was given by Nambu. The theories are accurate to terms of order $(m/M)^{1/2}$ where m is the mass of the electron and M the mass of the ion, and so give quite accurate quantitative accounts of the properties of both normal metals and super-conductors."]

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Annexure 1

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Theory of Superconductivity*

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A theory of superconductivity is presented, based on the fact that the interaction between electrons resulting from virtual exchange of phonons is attractive when the energy difference between the electron states involved is less than the phonon energy, $\hbar\omega$. It is favorable to form a superconducting phase when this attractive interaction dominates the repulsive screened Coulomb interaction. The normal phase is described by the Bloch individual-particle model. The ground state of a superconductor, formed from a linear combination of normal state configurations in which electrons are virtually excited in pairs of opposite spin and momentum, is lower in energy than the normal state by an amount proportional to an average $\langle\hbar\omega\rangle$, consistent with the isotope effect. A mutually orthogonal set of excited states in one-to-one correspondence with those of the normal phase is obtained by specifying occupation of certain Bloch states and by using the rest to form a linear combination of virtual pair configurations. The theory yields a second-order phase transition and a Meissner effect in the form suggested by Pippard. Calculated values of specific heats and penetration depths and their temperature variation are in good agreement with experiment. There is an energy gap for individual-particle excitations which decreases from about 3.5 kT_c at $T=0^\circ\text{K}$ to zero at T_c . Tables of matrix elements of single-particle operators between the excited-state superconducting wave functions, useful for perturbation expansion and calculations of transition probabilities, are given.

I. INTRODUCTION

THE main facts which a theory of superconductivity must explain are (1) a second-order phase transition at the critical temperature, T_c , (2) an electronic specific heat varying as $\exp(-T_c/T)$ near $T=0^\circ\text{K}$ and other evidence for an energy gap for individual particle-like excitations, (3) the Meissner-Ochsenfeld effect ($B=0$), (4) effects associated with infinite conductivity ($E=0$), and (5) the dependence of T_c on isotopic mass, $T_c\sqrt{M}=\text{const.}$ We present here a theory which accounts for all of these, and in addition gives good quantitative agreement for specific heats and penetration depths and their variation with temperature when evaluated from experimentally determined parameters of the theory.

When superconductivity was discovered by Onnes¹ (1911), and for many years afterwards, it was thought to consist simply of a vanishing of all electrical resistance below the transition temperature. A major advance was the discovery of the Meissner effect² (1933), which showed that a superconductor is a perfect diamagnet; magnetic flux is excluded from all but a thin penetration region near the surface. Not very long afterwards (1935), London and London³ proposed a phenomenological theory of the electromagnetic properties in which the diamagnetic aspects were assumed

basic. F. London⁴ suggested a quantum-theoretic approach to a theory in which it was assumed that there is somehow a coherence or rigidity in the superconducting state such that the wave functions are not modified very much when a magnetic field is applied. The concept of coherence has been emphasized by Pippard,⁵ who, on the basis of experiments on penetration phenomena, proposed a nonlocal modification of the London equations in which a coherence distance, ξ_c , is introduced. One of the authors^{6,7} pointed out that an energy-gap model would most likely lead to the Pippard version, and we have found this to be true of the present theory. Our theory of the diamagnetic aspects thus follows along the general lines suggested by London and by Pippard.⁸

The Sommerfeld-Bloch individual-particle model (1928) gives a fairly good description of normal metals, but fails to account for superconductivity. In this theory, it is assumed that in first approximation one may neglect correlations between the positions of the electrons and assume that each electron moves independently in some sort of self-consistent field determined by the other conduction electrons and the ions. Wave functions of the metal as a whole are designated by occupation of Bloch individual-particle states of energy $\epsilon(\mathbf{k})$ defined by wave vector $\mathbf{k}$ and spin σ ; in the ground state all levels with energies below the Fermi energy, ϵ_F , are occupied; those above are unoccupied. Left out of the Bloch model are correlations between electrons brought about by Coulomb forces and interactions between electrons and lattice vibrations (or phonons).

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